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None

(58) Field of search

C5D

(54) Granular detergent composition

(57) A granular detergent composition comprises by blending, in the powder form, (a) a granular detergent containing at least one alpha-sulfo fatty acid ester salt and (b) a granular stabilizer containing a carbonate and an acidic substance. The composition has granular or powder properties and suppresses hydrolysis of the alpha-sulfo fatty acid ester salt contained therein over a period of time.

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SPECIFICATION

Granular Detergent Composition

Background of the Invention

Field of the Invention

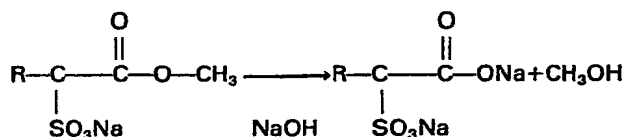
- 5 The present invention relates to a granular or powdered detergent composition containing an alpha-sulfo fatty acid ester salt. More specifically, it relates to a granular detergent composition having a suppressed hydrolyzable property of an alpha-sulfo fatty acid ester salt contained therein even when the granular detergent composition is stored for a long time. 5

Description of the Related Art

- 10 It is known in the art that various attempts have been made to develop a granular detergent composition having good granular or powder properties and good detergency, without using phosphate, since it is better to avoid the use of a phosphate in a detergent composition from the view point of pollution. One attempt heretofore made was to use a new builder in lieu of the phosphate, and another was to use, various surface active agents exhibiting good detergency. 10

- 15 Among these surface active agents, alpha-sulfo fatty acid ester salts are particularly notable since they have excellent detergency and also are not sensitive against calcium. Granular detergent compositions containing, as an active detergent component, these surface active agents are disclosed in, for example, Japanese Unexamined Patent Publication (Kokai) Nos. 47-6276 and 47-12582, as well as U.S. Patent No. 3338838. 15

- 20 The granular detergent compositions containing the above-mentioned alpha-sulfo fatty acid ester salts have, however, a disadvantage in that alpha-sulfo fatty acid ester salts are susceptible to hydrolysis during the production process or during storage. That is, alpha-sulfo fatty acid ester salts are inherently likely to be hydrolyzed and converted into alpha-sulfo fatty acid salts by cleavage of the ester linkage. The resultant alpha-sulfo fatty acid salts are only slightly soluble in water and have poor detergency. This hydrolysis mechanism is described, in detail, in, for example, W. Stein et. al., JACOS., 52, 329 (1974), showing that, when alpha-sulfo fatty acid ester salts are allowed to stand in an alkaline region, the di-salts are formed as follows: 20 25



wherein R represent an alkyl group.

- 30 To eliminate the above-mentioned problem, it is disclosed in, for example Japanese Unexamined Patent Publication No. 52-117908 that polyethylene glycol is added to a detergent slurry containing an alpha-sulfo fatty acid ester salt, thereby preventing the hydrolysis of the alpha-sulfo fatty acid ester salt during spray drying. It is also disclosed in Japanese Unexamined Patent Publication No. 50-151905 that (a) alpha-sulfo fatty acid ester salts contained in the granular detergent are susceptible to cleavage of the ester linkage during storage, and this cleavage of the ester linkage is promoted when the granular detergent is spray dried. This publication proposes the use of hindered phenolic compounds and hydroxy polycarbonic acid salts to prevent the above-mentioned cleavage of the ester linkage. 30 35

- Japanese Unexamined Patent Publication No. 52-28507 proposes the use of a specific alkaline builder in a granular detergent composition, since an alpha-sulfo fatty acid ester salt is susceptible to hydrolyzation in the presence of an alkaline builder such as sodium silicate over a period of time. 40

- However, the above-mentioned proposals do not completely solve the above-mentioned problems. Particularly, an improvement is desired in the tendency for granular detergents to be deteriorated over a period of time due to their insufficient storage stability. Furthermore, since an alkaline builder is an essential ingredient in a garment detergent, and is a necessary inclusion in view of the powder properties, there is a demand for a detergent composition in which a conventional alkaline builder and an alpha-sulfo fatty acid ester salt can be stably contained over a long period of time. In this regards, the problem of the prevention of the hydrolysis cannot be solved merely by the addition of an amount of the alkaline builder to the detergent composition or by separately adding the alkaline builder to a washing bath, because these methods lead only to a decrease in the detergent power or detergency and a deterioration of the powder properties. 45 50

Summary of the Invention

- Accordingly, the objects of the present invention are to eliminate the above-mentioned problems of the prior art and to provide a granular detergent composition having good granular or powder properties and having a suppressed hydrolyzable property of an alpha-sulfo fatty acid ester salt contained therein over a period of time. 55

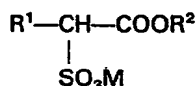
Other objects and advantages of the present invention will be apparent from the following description. In accordance with the present invention, there is provided a granular detergent composition

comprising by blending, in the powder form, (a) a granular detergent containing at least one alpha-sulfo fatty acid ester salt and (b) a granular stabilizer containing at least one carbonate and at least one acidic substance.

Description of the Preferred Embodiments

The present inventors have found that the hydrolysis of the alpha-sulfo fatty acid ester salt over a period of time can be effectively prevented by blending a granular detergent containing an alpha-sulfo fatty acid ester salt with a granular detergent containing both a carbonate and an acidic substance. Although the mechanism for preventing the hydrolysis of an alpha-sulfo fatty acid ester salt over a period of time is not clearly understood, it is believed that the carbonate and the acidic substance present in the granular stabilizer gradually react in the presence of a small amount of water to form gaseous carbon dioxide, and that the carbon dioxide thus formed then suppresses the hydrolysis of an alpha-sulfo fatty acid ester salt under an alkaline condition.

The preferable alpha-sulfo fatty acid ester salts usable in the present invention are those having the general formula (I):



(I)

wherein R¹ is an alkyl group having 4 to 20 carbon atoms, R² is an alkyl group having 1 to 6 carbon atoms, and M is Na, K, or NH₄.

The alpha-sulfo fatty acid ester salts can be produced by any conventional process. For example, a fatty acid ester derived from a fatty acid and a lower alcohol is sulfonated in a conventional thin-film type or vessel type sulfonation apparatus, followed by neutralization. Alternatively, a fatty acid is similarly sulfonated and the sulfonated product is then esterified with a lower alcohol, followed by neutralization. Examples of the starting fatty acids are fatty acids having the specified carbon atom number derived from natural fats and oils such as tallow fats, coconut oil, palm oil, and palm Kernel oil.

The granular detergents usable in the present invention preferably contain 1% to 30% by weight of the alpha-sulfo fatty acid ester salt or salts. The granular detergent composition according to the present invention may contain, in addition to the above-mentioned alpha-sulfo fatty acid ester salt, other surfactants, builders, and the like.

Examples of the other surfactants are anionic surfactants such as alkylbenzene sulfonates, alkyl sulfonates, alpha-olefin sulfonates, alkyl sulfates, alkyl polyether sulfates, and fatty acid soaps; nonionic surfactants such as alkyl ethoxylates, alkylphenyl ethoxylates, and alkylalkanol amides; and ampholytic surfactants such as alkyl betains. Examples of the builders are inorganic builders such as sodium silicate, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, sodium pyrophosphate, zeolites, and sodium sulfates; and organic builders such as sodium citrate, sodium ethylenediamine tetraacetate, and sodium nitrilotriacetate. Other conventional ingredients such as polyethyleneglycols, carboxymethylcellulose, enzymes, perfumes, and dyes may be contained in the granular detergents according to the present invention.

The granular detergent usable as a component (a) in the present invention can be obtained, for example, by spray drying an aqueous slurry containing the above-mentioned detergent ingredients, or by granulating a composition containing the above-mentioned detergent ingredients. The preferable powder particle size of the granular detergent used as a component (a) of the present invention is 100 to 1000 μm.

The granular stabilizers usable in the present invention are those containing both a carbonate and an acidic substance therein. The carbonates usable in the present invention are those which are decomposed to generate carbon dioxide. Typical examples of such carbonates are sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, and calcium carbonate. These carbonates can be used alone or in any mixture thereof. The preferable carbonates are sodium carbonate and sodium bicarbonate.

The acidic substances usable in the present invention are those having an acidity such that the acidic substance is reacted with the carbonate in the presence of water to generate carbon dioxide. The preferable acidic substances are those which are solid at an ambient or ordinary temperature. Typical examples of the acidic substances are carboxylic acids such as citric acid, malic acid, tartaric acid, and polyacrylic acid; amino carboxylic acids such as nitrilotriacetic acid and ethylenediamine tetraacetic acid; sulfamic acid; p-toluene sulfonic acid; and sodium bisulfate.

Although there is no specific limitation in the compounding ratio of the carbonate and the acidic substance in the granular stabilizers, a ratio of the carbonate to the acidic substance in the granular stabilizer is preferably 10/1 to 1/10.

The granular stabilizers usable in the present invention can optionally contain, in addition to the essential carbonate and acidic substance, solid granulation additives such as sodium sulfate, white carbon, and zeolite, and binders such as polyethylene glycol, glycerol, carboxymethyl cellulose, and water.

Furthermore, the presence of a small amount of water in the granular stabilizer is preferable for effectively allowing the action or function of the granular stabilizer. Although the water transferred from the granular detergent can be also utilized, the previous inclusion of water in the granular stabilizer, preferably in an

amount of 0.1 to 10% by weight, is preferable. The preferable particle diameter of the granular stabilizer is approximately 100 to 1000 μm .

The granular stabilizers usable in the present invention can be prepared, for example, as follows. That is, the carbonate and the acidic substance are separately finely divided into those having a particle size of approximately 50 to 300 μm . The resultant finely divided particles of the carbonate and the acidic substance are mixed together, after uniforming the particle size thereof. During this granulating step, the amount of water in the granular stabilizer can be controlled by the addition or drying of water. Furthermore, the flowability of the granular stabilizer can be improved by the addition of a finely divided inorganic material such as zeolite, after granulation.

The granular detergent composition according to the present invention can be prepared by powder blending the above-mentioned granular detergent and granular stabilizer in any conventional manner. The preferable blending ratio of the granular stabilizer is 1 to 20 parts by weight based on 100 parts by weight of the granular detergent.

According to the present invention, the hydrolysis of the alpha-sulfo fatty acid ester salts with the lapse of time is effectively prevented by the generation of carbon dioxide, which is caused by the gradual reaction of the granular stabilizer during the storage thereof.

Examples

The present invention now will be further illustrated by, but is by no means limited to, the following examples.

20 Examples 1 to 9 and Comparative Examples 1 to 3 20

A granular detergent having the following composition and having an average particle diameter of 400 μm was prepared by a spray drying method.

	Ingredient	% by weight	
25	Sodium α -sulfo hydrogenated tallow fatty acid methylester	20	25
	Sodium silicate (JIS #2, $\text{SiO}_2/\text{Na}_2\text{O}=2.7$)	10	
	Synthetic type A zeolite (Silitone B, Mizusawa Industrial Chemicals, Ltd.)	20	
	Water	4	
30	Sodium sulfate	balance	30

The granular stabilizers were prepared as follows:

That is, the carbonate listed in Table 1 and the acidic substances listed in Table 1 were separately ground to obtain substances having an average particle diameter of approximately 100 μm . The resultant carbonate and acidic substance were uniformly mixed together. To the resultant mixture, 5 parts, based on 90 parts of the mixture, of water as a binder was sprayed and was granulated in a disc type spray tower. After the granulation, the powdered synthetic zeolyte was added to the granules to prepare the granular stabilizers having the following compositions and having an average particle diameter of 350 μm .

	Ingredient	% by weight	
	Carbonate	45	
40	Acidic substance	45	40
	Water	5	
	Synthetic type A zeolite (Silitone B)	5	

Granular detergent compositions of Examples 1 to 9 were obtained by compounding 5 parts by weight of the granular stabilizers containing the carbonates and the acidic substances listed in Table 1 to 100 parts by weight of the granular detergent prepared above. In addition, as comparative examples, a granular detergent composition containing no granular stabilizer (i.e., Comparative Example 1), a granular detergent composition containing only sodium bicarbonate (i.e., Comparative Example 2), and a granular detergent composition containing only citric acid (i.e., Comparative Example 3) were prepared.

The increased ratios of hydrolysis of these compositions were determined as follows:

50 The total amount of the surfactants was determined by a conventional methylene blue back titration 50

method and the total amount M of the salt of alpha-sulfo fatty acid ester and the disalt of alpha-sulfo fatty acid were calculated from the predetermined compounding ratio of the surfactants. Then, the detergent composition was treated with a 90% ethanol solution at a temperature of 50°C under pH of 11. Thus, the disalt of alpha-sulfo fatty acid was separated as an insoluble matter. The amounts of the disalt was
5 determined by a conventional methylene blue back titration method after dissolving the disalt in a 50% ethanol solution. 5

The hydrolysis rate D was determined from the following equation:

$$D = \frac{S}{M} \times 100$$

The hydrolysis rates immediately after the preparation and after allowing the solution to stand for one
10 month at a temperature of 35°C were determined and the increased rate of the hydrolysis was calculated as follows: 10

Increased rate of hydrolysis = (Hydrolysis rate after one month) - (Hydrolysis rate immediately after the production).

The results are shown in Table 1.

TABLE 1

Example No.	Example (Present Invention)									Example (Comparative)		
	1	2	3	4	5	6	7	8	9	1	2	3
Carbonate	Sodium bicarbonate	Sodium bicarbonate	Sodium bicarbonate	Sodium bicarbonate	Sodium bicarbonate	Sodium carbonate	Calcium carbonate	Potassium carbonate	Potassium bicarbonate	Sodium bicarbonate (350 μ m)	None	None
Acidic substance	Citric acid	Sodium bisulfate	Ethylene diamine tetraacetic acid	Nitrilo-triacetic acid	Malic acid	Citric acid	Citric acid	Citric acid	Citric acid	None	Citric acid	None
Amount of addition (%)	5	5	5	5	5	5	5	5	5	5	5	—
Increased rate of hydrolysis (%)	15	20	20	20	17	18	20	18	15	40	30	40

CLAIMS

1. A granular detergent composition comprising by blending, in the powder form, (a) a granular detergent containing at least one alpha-sulfo fatty acid ester salt and (b) a granular stabilizer containing at least one carbonate and at least one acidic substance.

- 5 2. A granular detergent composition as claimed in claim 1, wherein the alpha-sulfo fatty acid ester salt has the general formula (I): 5



wherein R¹ is an alkyl group having 4 to 20 carbon atoms, R² is an alkyl group having 1 to 6 carbon atoms, and M is Na, K, or NH₄.

- 10 3. A granular detergent composition as claimed in claim 1, wherein the alpha-sulfo fatty acid ester salt is contained in an amount of 1% to 30% by weight in the granular detergent. 10

4. A granular detergent composition as claimed in claim 1, wherein a ratio of the carbonate to the acidic substance in the granular stabilizer is 10/1 to 1/10.

- 15 5. A granular detergent composition as claimed in claim 1, wherein the carbonate is sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, or calcium carbonate. 15

6. A granular detergent composition as claimed in claim 1, wherein the acidic substance is citric acid, malic acid, tartaric acid, polyacrylic acid, nitrilotriacetic acid, ethylenediamine tetraacetic acid, sulfamic acid, p-toluene sulfonic acid, or sodium bisulfate.

- 20 7. A granular detergent composition as claimed in claim 1, wherein the amount of the granular stabilizer is 1 to 20 parts by weight based on 100 parts by weight of the granular detergent. 20

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